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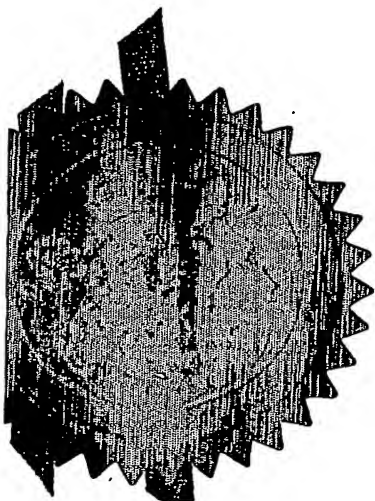
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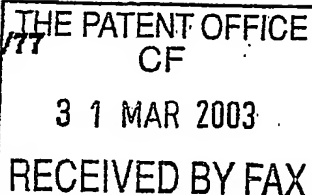
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*Andrew Gersey*

Dated

24 June 2004





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P01/7700 0.03-0307290.7

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# Request for grant of a patent

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1. Your reference

MDX;001-P-UK

2. Patent application number  
(The Patent Office will fill in this part)

0307290.7

31 MAR 2003

3. Full name, address and postcode of the or of each applicant (underline all surnames)

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Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

7928138001

4. Title of the invention

ENHANCING SILVER TARNISH-RESISTANCE

5. Name of your agent (if you have one)

PAUL GILBERT COLE

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

Lucas & Co.  
135 Westhall Road  
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Surrey  
CR6 9HJ  
05815709001 ✓

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6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number  
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Date of filing  
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7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing  
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

- a) any applicant named in part 3 is not an inventor, or
- b) there is an inventor who is not named as an applicant, or
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See note (d))

Yes

# Patents Form 1/77

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## Continuation sheets of this form

Description	21 ✓
Claim(s)	3 ✓
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CP

10. If you are also filing any of the following, state how many against each item.

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### Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77) 1 + 2

Request for preliminary examination and search (Patents Form 9/77)

Request for substantive examination (Patents Form 10/77)

Any other documents (please specify)

11.

I/We request the grant of a patent on the basis of this application.

Signature

Date

Paul Cole

31 Mar 03

12. Name and daytime telephone number of person to contact in the United Kingdom

Paul Cole - 01883 626211

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Patents Form 1/77

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- 1 -

## ENHANCING SILVER TARNISH-RESISTANCE

### FIELD OF THE INVENTION

5       The present invention relates to the use of organo-sulphur compounds in the enhancement of the tarnish resistance of silver alloys, to silver articles of enhanced tarnish resistance that have been surface-treated with the organo-sulphur compounds and to methods of keeping and display of the treated articles.

### 10       BACKGROUND TO THE INVENTION

Standard Sterling silver provides manufacturers and silversmiths with a versatile and reliable material but it is inevitable that finished articles will require further cleaning and polishing to temporarily remove undesired tarnish products.  
15   It is a well-known fact that with exposure to everyday atmospheric conditions, silver and silver alloys develop a lustre-destroying dark film known as tarnish.

Since ancient times it has been appreciated that unalloyed 'fine' silver is too soft to withstand normal usage, and it has been the practice to add a proportion of a base metal to increase hardness and strength. In the UK,  
20   legislation that has existed since the fourteenth century specifies a minimum silver content of articles for sale at 92.5% (the Sterling standard), but does not specify the base metal constituents. Experience convinced early silversmiths that copper was the most suitable of the metals available to them. Modern silver-sheet manufacturers generally adhere to this composition, although sometimes a  
25   proportion of copper is replaced by cadmium to attain even greater ductility. Sterling with a 2.5% cadmium content is a standard material for spinning and stamping. Lower grades of silver alloys are common in many parts of Europe for the production of hollow-ware and cutlery. The 800-grade alloys (Ag parts per  
30   thousand) are predominantly used in southern and mid-Europe whereas in Scandinavia the 830 standard is predominant.

In all but the largest manufacturing companies, most of the annealing and soldering required to assemble finished or semi-finished articles is carried out with the flame of an air-gas blowtorch. The oxidising or reducing nature of the flame and the temperature of the articles are controlled only by the skill of the silversmith. Pure silver allows oxygen to pass easily through it, particularly when the silver is heated to above red heat. Silver does not oxidise in air, but the copper in a silver/copper alloy is oxidised to cuprous or cupric oxide. Pickling of the oxidised surface of the article in hot dilute sulphuric acid removes the superficial but not the deeper seated copper oxide so that the surface consists of fine or unalloyed silver covering a layer of silver/copper oxide mixture. The pure silver is easily permeated during further heating, allowing copper located deeper below the surface to become oxidised. Successive annealing, cold working and pickling produces a surface that exhibits the pure lustre of silver when lightly polished but with heavier polishing reveals dark and disfiguring stains known as 'fire-stain' or 'fire'. Soldering operations are much more productive of deep fire-stain because of the higher temperatures involved. When the depth of the fire-stain exceeds about 0.025mm (0.010 inches) the alloy is additionally prone to cracking and difficult to solder because an oxide surface is not wetted by solder so that a proper metallurgical bond is not formed.

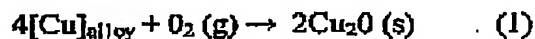
Patent GB-B-2255348 (Rateau, Albert and Johns; Metalcurop Recherche) disclosed a novel silver alloy that maintained the properties of hardness and lustre inherent in Ag-Cu alloys while reducing problems resulting from the tendency of the copper content to oxidise. The alloys were ternary Ag-Cu-Ge alloys containing at least 92.5 wt% Ag, 0.5-3 wt% Ge and the balance, apart from impurities, copper. The alloys were stated to be stainless in ambient air during conventional production, transformation and finishing operations, to be easily deformable when cold, to be easily brazed and not to give rise to significant shrinkage on casting. They were also stated to exhibit superior ductility and tensile strength and to be annealable to a required hardness. Germanium was stated to exert a protective function that was responsible for the advantageous

combination of properties exhibited by the new alloys, and was in solid solution in both the silver and the copper phases. The microstructure of the alloy was said to be constituted by two phases, a solid solution of germanium and copper in silver surrounded by a filamentous solid solution of germanium and silver and copper. The germanium in the copper-rich phase was said to inhibit surface oxidation of that phase by forming a thin  $\text{GeO}$  or  $\text{GeO}_2$  protective coating which prevented the appearance of fire-stain during brazing and flame annealing which results from the oxidation of copper at high temperatures. Furthermore the development of tarnish was appreciably delayed by the addition of germanium, the surface turned slightly yellow rather than black and tarnish products were easily removed by ordinary tap water. The alloy was said to be useful *inter alia* in jewellery. However, the alloy disclosed in the above patent suffers limitations insofar as it can exhibit large grain size, leading to poor deformation properties and formation of large pools from low-melting eutectics resulting in localised surface melting when the alloy is subject to the heat of an air torch.

Patents US-A-6168071 and EP-B-0729398 (Johns) disclosed a silver/germanium alloy which comprised a silver content of at least 77 wt % and a germanium content of between 0.4 and 7%, the remainder principally being copper apart from any impurities, which alloy contained elemental boron as a grain refiner at a concentration of greater than 0ppm and less than 20ppm. The boron content of the alloy could be achieved by providing the boron in a master copper/boron alloy having 2 wt % elemental boron. It was reported that such low concentrations of boron surprisingly provided excellent grain refining in a silver/germanium alloy, imparting greater strength and ductility to the alloy compared with a silver/germanium alloy without boron. The boron in the alloy inhibited grain growth even at temperatures used in the jewellery trade for soldering, and samples of the alloy were reported to have resisted pitting even upon heating repeatedly to temperatures where in conventional alloys the copper/germanium eutectic in the alloy would melt. Strong and aesthetically pleasing joints between separate elements of the alloy could be obtained without

using a filler material between the free surfaces of the two elements and a butt or lap joint could be formed by a diffusion process or resistance or laser welding techniques. Compared to a weld in Sterling silver, a weld in the above-described alloy had a much smaller average grain size that improved the formability and ductility of the welds, and an 830 alloy had been welded by plasma welding and polished without the need for grinding.

Ternary and quaternary alloys e.g. Ag-Cu-Ge alloys and Ag-Cu-Zn-Ge alloys include two base metal alloying elements, Cu and Ge, in a noble parent metal, Ag. On exposure to an oxidising atmosphere, two oxidation reactions have to be considered. Firstly, the oxidation of copper to cuprous oxide:



Secondly, the oxidation of germanium to germanium (di)oxide:



Under standard conditions, i.e. for pure Cu and pure Ge each reacting with pure oxygen gas at 1 atm pressure to form the pure oxide phase, both reactions are feasible, with the chemical driving force for reaction (2) being higher than that of reaction (1) by a factor of 1.65.

Various proposals have been made for cleaning or protecting Sterling silver and other known grades of silver to remove tarnish and/or to inhibit the formation of tarnish.

According to WO 02/095082 (Johns) tarnish resistance of ternary alloys of silver, copper and germanium or quaternary alloys of silver, copper, zinc and germanium can be increased by casting a molten mixture to form the alloy and annealing the alloy to reduce its thickness and re-crystallize the grains in the alloy, the annealing being carried out under a selectively oxidizing atmosphere e.g.  $\text{H}_2/\text{H}_2\text{O}$  or  $\text{CO}/\text{CO}_2$  to promote the formation of  $\text{GeO}_2$  while preventing the formation of  $\text{Cu}_2\text{O}$ .

GB-A-1130540 is concerned with the protection of a finished surface of Sterling or Britannia silver as a step in a production run, and discloses a process that comprises the steps of:

5 wetting a clean silver surface of an article with a solution comprising 99 parts by weight of a volatile organic solvent, for example trichloroethylene or 1,1,1-trichloroethane and from 0.1-1.8 parts by weight of an organic solute containing a -SH group and capable of forming a transparent colourless protective layer on the silver surface, for example stearyl and cetyl mercaptan or thioglycollate;

10 allowing the solution to react with the surface to form such a layer and allowing the solvent to evaporate; and

washing the surface with a detergent solution, rinsing the surface with hot water and allowing it to dry.

15 The above process is stated to provide a "long-term finish" intended to last the intended shelf-life until the article reaches the user.

Treatments of the above kind are believed to result in the formation of a self-assembled coating derived from the thiol compounds in which the sulphur  
20 atoms are bound onto the metal surface and the alkyl tails are directed away from the metal surface, see US-A-6183815 (Enick). Yousong Kim *et al*, <http://www.electrochem.org/meetings/past/200/abstracts/symposia/h1/1026.pdf> reported that the adsorption of thiols onto silver proceeds through an anodic oxidation reaction that produces a shift of the open circuit potential of the  
25 substrate metal in the negative direction or if the potential is fixed an anodic current peak:



Kwan Kim, *Adsorption and Reaction of Thiols and Sulfides on Noble Metals*, Raman SRS-2000, 14-17 August 2000, Xiamen, Fujian, China,  
30 <http://pcoss.org/icorsxm/paper/kuankim.pdf>, also discloses the formation of self-assembled monolayers and discloses that alkanethiols, dialkyl sulfides and dialkyl



disulfides self-assemble on silver surfaces with aliphatic dithiols forming dithiolates by forming two Ag-S bonds. In contrast, the literature on formation of alkylthiols of germanium is relatively sparse. The reaction of alkanethiols with Ge to form a high quality monolayer has been reported in the context of semiconductor and nanotechnology by Han *et al*, *J. Am. Chem. Soc.*, 123, 2422 (2001). In the experiment described, a Ge(111) wafer is sonicated in acetone to dissolve organic contaminants and immersed in concentrated HF to remove residual oxide and produce a hydrogen-terminated surface, after which the wafer is immersed in an alkanethiol solution in isopropanol, sonicated in propanol and dried.

### SUMMARY OF THE INVENTION

Although GB-A-1130540 was alleged to provide a long-term finish, in the inventor's experience this type of treatment does not fully solve the difficulties created by tarnish in the period between manufacture and supply to the ultimate purchaser or user and suffers from a number of shortcomings. Although a silver product might arrive at the retailer in an untarnished state, it was largely the result of the wrapping applied by the manufacturer, which protected the article from air. Once the wrapping was removed and the article was displayed in a retail environment such as a display case in a hotel where it was subject to ambient air and the heat of artificial lighting, an article of conventional Sterling silver would require re-polishing after one week and after two weeks would normally be so tarnished as to be un-saleable. At an exhibition, the life of an article on display before significant tarnish sets in may be as short as 3-4 days. Re-polishing produces wear and fine handling scratches, so that unless the article can be sold quickly it loses its pristine appearance. The need to polish display silver at frequent intervals adds to the labour cost of a jeweller or other retail establishment, whose management take the view that its staff should be employed to sell products and not to clean stock. Tarnish at point of sale is therefore a

serious problem that reduces the willingness of those in the distribution chain to stock and display silver products, and which has not yet been adequately solved.

When the product reaches the ultimate purchaser, it is of course desirable that the task of tarnish removal should be made as infrequent and undemanding as possible.

Silver alloys according to the teaching of GB-B-2255348 and EP-B-0729398 are now commercially available in Europe and in the USA under the trade name Argentium, and the word "Argentium" as used herein refers to these alloys. Although they exhibit improved tarnish resistance compared to c.g. Sterling silver, and any tarnish that forms can be removed by simple washing, there is still room for improvement in tarnish resistance. That remains true even when annealing is conducted in a selectively oxidising atmosphere as disclosed in WO 02/095082.

It has now been found that an alkanethiol, alkyl thioglycollate, dialkyl sulphide or dialkyl disulphide can be used for the surface treatment of an alloy of silver containing an amount of germanium that is effective to reduce fire-stain and/or tarnishing so as to reduce or further reduce tarnishing of the alloy such that a sample can be subjected to hydrogen sulphide gas above a 20% solution of ammonium polysulphide for at least 30 minutes and typically 45-60 minutes while retaining a generally untarnished appearance.

The invention also therefore relates to the use of an organic compound containing -SH or -S-S- bonds e.g. a C<sub>12</sub>-C<sub>24</sub> alkanethiol, alkyl thioglycollate, dialkyl sulphide or dialkyl disulphide in the preparation of a tarnish inhibitor for an article of a silver/germanium alloy that has a silver content of at least 77 wt % and a germanium content of between 0.1 and 7% so as to reduce tarnishing of said alloy such that a sample can be supported close above a 20% solution of

ammonium polysulphide for at least 30 minutes and typically 45-60 minutes while retaining a generally untarnished appearance.

5 The invention further provides an alloy of silver, or a shaped article formed of said alloy, containing an amount of germanium that is effective to reduce fire-stain and/or tarnishing and that has been treated with a C<sub>12</sub>-C<sub>24</sub> alkanethiol, alkyl thioglycollate, dialkyl sulphide or dialkyl disulphide.

10 The invention further provides a method for manufacturing a tarnish-resistant silver article, which comprises the steps of:

forming a shaped article of an alloy of silver containing an amount of germanium that is effective to reduce fire-stain and/or tarnishing;

surface treating the article with an alkanethiol, alkyl thioglycollate, dialkyl sulphide or dialkyl disulphide; and

15 introducing the article into packaging.

The above accelerated tarnish test in which the article is subject to hydrogen sulphide gas from the ammonium polysulphide solution above which it is suspended at a height of e.g. 30mm corresponds to a period of a year or more in  
20 a retail environment where an article is on display and exposed to ambient atmosphere and may be subject to elevated temperatures. It is the combination of the protective function of the germanium content of the alloy with the further protection from the organo-sulphur compound that is believed to be responsible for the observed increase in tarnish resistance. The period during which the article  
25 retains its untarnished appearance under these severe conditions may be three or more times the corresponding period for an article that has not been treated with an organo-sulphur compound, which is unexpected because the same accelerated tarnish test carried out under the same conditions on a conventional Sterling silver article not containing protective germanium does not reveal a significant increase  
30 in untarnished lifetime between its untreated and organo-sulfur treated states.

Accelerated tarnishing tests with Argentium Sterling using ammonium polysulphide have been reported by the Society of American Silversmiths, see

<http://www.silversmithing.com/largentium4.htm>

and in a comparative test the Argentium Sterling remained untarnished after one  
5 hour whereas conventional Sterling became tarnished after less than 15 minutes.  
However, in this test 0.5ml of 20% ammonium polysulfide solution is mixed with  
200ml of distilled water, so that the test is greatly less severe than when samples  
are exposed to the 20% solution itself. In WO 02/095082, samples were  
suspended above 20% ammonium polysulphide, but the exposure times were  
10 relatively short, and onset of yellowing was reported for Ag-Cu-Ge alloys after 3-  
5 minutes exposure. Other tests reported in that specification involve placing  
samples in a desiccator containing flowers of sulphur and calcium nitrate and are  
less severe than the ammonium polysulphide test.

15

#### DETAILED DESCRIPTION OF THE INVENTION

The alloys that may be treated according to the invention include an alloy  
of silver containing an amount of germanium that is effective to reduce fire-stain  
and/or tarnishing. US-A-6406664 (Diamond) discloses that amounts of  
20 germanium as low as 0.1wt% can be effective provided that substantial amounts  
of tin are present but although formulation examples are given, no test data for  
corrosion or fire-stain is given either for articles made by casting or for articles  
fabricated from sheet. The inventor considers that 0.5 wt% Ge provides a  
preferred and more realistic lower limit and that in practice use of less than 1wt%  
25 is undesirable. A two-component copper-free alloy could comprise 99% Ag and 1  
% Ge, and a tarnish-free casting alloy for jewellery has been reported that  
comprises 2.5%Pt, 1% Ge, balance Ag and optionally containing Zr, Si or Sn.

The ternary Ag-Cu-Ge alloys and quaternary Ag-Cu-Zn-Ge alloys that can  
30 suitably be treated by the method of the present invention are those having a  
silver content of at least 30%, preferably at least 60%, more preferably at least

80%, and most preferably at least 92.5%, by weight of the alloy, up to a maximum of no more than 98%, preferably no more than 97%. The germanium content of the Ag-Cu- (Zn)-Ge alloys should be at least 0.1%, preferably at least 0.5%, more preferably at least 1.1%, and most preferably at least 1.5%, by weight of the alloy, up to a maximum of preferably no more than 6.5%, more preferably no more than 4%. If desired, the germanium content may be substituted, in part, by one or more elements which have an oxidation potential selected from Al, Ba, Be, Cd, Co, Cr, Er, Ga, In, Mg, Mn, Ni, Pb, Pd, Pt, Si, Sn, Ti, V, Y, Yb and Zr, provided the effect of germanium in terms of providing fire-stain and tarnish resistance is not unduly adversely affected. The weight ratio of germanium to substitutable elements may range from 100: 0 to 60: 40, preferably from 100: 0 to 80: 20. Preferably, the germanium content consist entirely of germanium, i. e. the weight ratio is 100: 0.

The remainder of the ternary Ag-Cu-Ge alloys, apart from impurities and any grain refiner, will be constituted by copper, which should be present in an amount of at least 0.5%, preferably at least 1%, more preferably at least 2%, and most preferably at least 4%, by weight of the alloy. For an '800 grade' ternary alloy, for example, a copper content of 18.5% is suitable. The remainder of the quaternary Ag-Cu-Zn-Ge alloys, apart from impurities and any grain refiner, will be constituted by copper which should be present in an amount of at least 0.5%, preferably at least 1%, more preferably at least 2%, and most preferably at least 4%, by weight of the alloy, and zinc which should be present in a ratio, by weight, to the copper of no more than 1: 1. Therefore, zinc is optionally present in the silver-copper alloys in an amount of from 0 to 100 % by weight of the copper content. For an '800 grade' quaternary alloy, for example, a copper content of 10.5% and zinc content of 8% is suitable.

In addition to silver, copper and germanium, and optionally zinc, the alloys preferably contain a grain refiner to inhibit grain growth during processing of the alloy. Suitable grain refiners include boron, iridium, iron and nickel, with

boron being particularly preferred. The grain refiner, preferably boron, may be present in the Ag-Cu-(Zn)-Ge alloys in the range from 1 ppm to 100 ppm, preferably from 2 ppm to 50 ppm, more preferably from 4 ppm to 20 ppm, by weight of the alloy.

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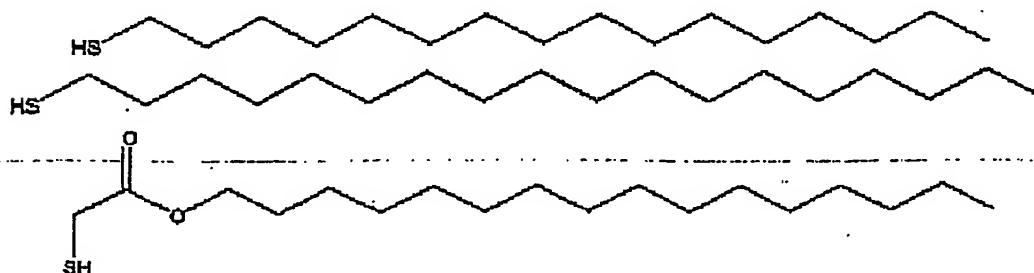
In a preferred embodiment, the alloy is a ternary alloy consisting, apart from impurities and any grain refiner, of 80% to 96% silver, 0.1 % to 5% germanium and 1 % to 19.9% copper, by weight of the alloy. In a more preferred embodiment, the alloy is a ternary alloy consisting, apart from impurities and grain refiner, of 92.5% to 98% silver, 0.3% to 3% germanium and 1% to 7.2% copper, by weight of the alloy, together with 1 ppm to 40 ppm boron as grain refiner. In a further preferred embodiment, the alloy is a ternary alloy consisting, apart from impurities and grain refiner, of 92.5% to 96% silver, 0.5% to 2% germanium, and 1% to 7% copper, by weight of the alloy, together with 1 ppm to 40 ppm boron as grain refiner.

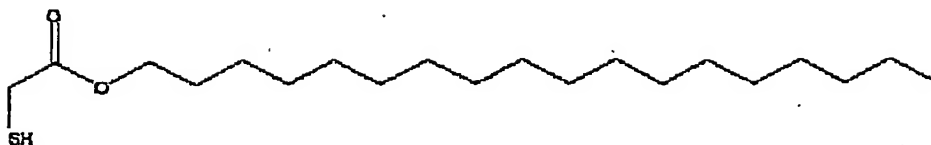
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As protective agent there may be used a compound containing a long chain alkyl group and a -SH or -S-S- group, e.g. an alkanethiol, dialkyl sulfide or dialkyl disulfides in which the chain is preferably at least 10 carbon atoms long and may be C<sub>12</sub>-C<sub>24</sub>. The -SH or -S-S- compounds that may be used include straight chain saturated aliphatic compounds containing 16-24 carbon atoms in the chain, for example stearyl mercaptan, cetyl mercaptan (octadecyl mercaptan) and stearyl and cetyl thioglycollates whose formulae appear below.

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Stearyl mercaptan is a white to pale yellow waxy solid that is insoluble in water. The protective agent may be used in solution in a solvent e.g. a non-polar organic solvent such as an alcohol e.g. methyl or ethyl alcohol, a ketone e.g. acetone or methyl ethyl ketone, an ether e.g. diethyl ether, an ester e.g. n-butyl acetate, a hydrocarbon, a halocarbon e.g. methylene chloride, 1,1,1-trichloroethane, trichloroethylene, perchloroethylene or HCFC 141b. The protective agent may comprise 0.1-1 wt% of the solvent. Solvents based on n-propyl bromide are presently preferred on the ground of the short atmospheric life of that compound, its relatively low toxicity compared to other halocarbons, its favourable chemical and physical properties and its boiling point, specific heat and latent heat of vaporization.

US-A-5616549 discloses a solvent mixture comprising: 90 percent to about 96.5 percent n-propyl bromide; 0 percent to about 6.5 percent of a mixture of terpenes, the terpene mixture comprising 35 percent to about 50 percent cis-pinane and 35 percent to about 50 percent trans-pinane; and 3.5 percent to about 5 percent of a mixture of low boiling solvents, the low boiling solvent mixture comprising 0.5 percent to 1 percent nitromethane, 0.5 percent to 1 percent 1,2-butylene oxide and 2.5 percent to 3 percent 1,3-dioxolane. The solvent mixture has the following advantages:

(i) it is properly stabilized against any free acid that might result from oxidation of the mixture in the presence of air, from hydrolysis of the mixture in the presence of water, and from pyrolysis of the mixture under the influence of high temperatures;

(ii) it is non-flammable and non-corrosive;

(iii) the various components of the solvent mixture are not regulated by the U.S. Clean Air Act; and

(iv) none of the various components of the solvent mixture are known cancer causing agents (i.e., the various components are not listed by N.T.I., I.A.R.C. and California Proposition 65, nor are they regulated by OSHA). Moreover, the solvent mixture has a high solvency with a kauri-butanol value  
5 above 120 and, more preferably, above 125. In addition, the solvent mixture has an evaporation rate of at least 0.96 where 1,1,1-Trichloroethane=1. Upon evaporation, the solvent mixture leaves a non-volatile residue (NVR) of less than 2.5 mg and, more preferably, no residue. Solvents made in accordance with the above patent are available from Enviro-Tech International, Inc of Melrose Park,  
10 Illinois, USA under the trade name EnSolv.

The surface treatment may be carried out after the manufacturing stages for a shaped article made of the alloy have been completed. The article may be of flatware, hollowware or jewellery. Fabrication steps may include spinning,  
15 pressing, forging, casting, chasing, hammering from sheet, planishing, joining by soldering brazing or welding, annealing and polishing using buffs/mops and aluminium oxide or rouge. An article to be treated may be de-greased ultrasonically in a treatment bath, dipped into a bath containing the treatment agent e.g. 1 wt% stearyl mercaptan in solvent e.g. EnSolv, rinsed in one or more  
20 baths of the solvent and allowed to dry by evaporation. The solvent should leave no or substantially no residue, so that subsequent washing with water or aqueous solvents should be unnecessary and the article can be allowed to dry. The article may then be packed for delivery into the distribution chain. This may include wrapping the article in one or more protective sheets, placing it in a presentation  
25 box, and wrapping the presentation box in a protective wrapping e.g. of heat-shrunk plastics film. Articles which have been treated with an organic compound containing -SH or -S-S- groups as aforesaid and packaged should not only reach their point of sale in good condition but should if displayed e.g. on a shelf or in a cabinet for an extended period, expected to be at least 6 months and possibly 12  
30 months or more, remain without development of significant tarnish.



For many purposes, e.g. light industrial applications, it may be preferred to carry out the anti-tarnish treatment using a predominantly aqueous solvent system. For this purpose, the protective agent may be dissolved in a water-immiscible organic solvent, for example a solvent based on *n*-propyl bromide, the  
5 resulting solution may be mixed with a relatively concentrated water-based soap or detergent composition which acts as a "carrier", after which water is added to the resulting mixture to provide an aqueous treatment dip or combined degreasing and treatment solution. Thus an aqueous dip has the advantages that a solvent degreasing system is not necessary, the dip is easily made and may be used cold,  
10 all areas of immersed articles can come into contact with the stearyl mercaptan or other treatment agent, Argentium Silver only requires 2 minutes in the dip, rinsing and drying of articles are made easy as water droplets are repelled from the surface of the polished silver, and the dip can be easily used in a manufacturing environment before articles are sent to retailers.

15

Preferred water-based detergents may be based on anionic, alkoxylated non-ionic or water-soluble cationic surface active agents or mixtures of them and preferably have a pH at or close to 7. Anionic surfactants may be based on alkyl sulphates and alkyl benzene sulphonates, whose harshness on prolonged skin  
20 exposure may be reduced by the co-presence or use of alkyl ethoxy sulphates (US-A-3793233, Rose *et al.*; 4024078 Gilbert; 4316824 Pancherni). Other known surfactants e.g. betaines may also be present, see e.g. US-A-4555360 (Bissett). A suitable formulation containing 5-15 wt% non-ionic surfactants and 15-30 wt% anionic surfactants is available commercially in the UK under the trade name  
25 Fairy Liquid (Proctor & Gamble).

An aqueous liquid may also be made by dissolving the treatment agent in a non-organic solvent and adding a relatively concentrated aqueous detergent liquid, for example undiluted Fairy Liquid. This provides a detergent liquid that  
30 has a number of advantages: the soapy liquid is easily made, the liquid is easily applied to the Argentium Silver articles with a damp sponge/cotton wool/cloth

etc, the liquid and lather enables the stearyl mercaptan or other treatment agent to get into those awkward areas on an article where a cloth may not be able to reach, rinsing and drying of articles are made easy as water droplets are repelled from the surface of the polished silver, the process can be easily used in a manufacturing environment before articles are sent to retailers and can also be easily used in a retail or domestic environment.

The articles may alternatively simply be polished with a polish containing 1-5wt% of the organo-sulphur compound e.g. stearyl mercaptan together with surfactants and a cleaning agent e.g. diatomaceous earth in a solvent. As a further alternative, they may be simply polished with a cloth impregnated with the organo-sulphur compound e.g. stearyl mercaptan. The advantages of a cleaning cloth are that it is easily manufactured, can be easily used in a retail or domestic environment and is good for general upkeep of Argentium Silver (if required).

The invention will now be further described, by way of illustration only, with reference to the following examples. Throughout the examples, the term "enhanced tarnish resistance" of samples treated with stearyl mercaptan refers to the comparison with samples of Argentium Silver which have not had any treatment except for polishing and cleaning in EnSolv 765.

#### Example 1

##### Solvent dip application (solvent degreased samples)

Solutions were made up containing stearyl mercaptan (0.1, 0.5 and 1.0 gram) in EnSolv 765 (100 ml). Samples of Argentium Sterling which had been polished and ultrasonically degreased in EnSolv 765 for 2 minutes were each immersed in one of the stearyl mercaptan solutions for periods of 2 minutes, 5 minutes and 15 minutes. The samples were then buffed with clean cotton wool.

In order to evaluate tarnish resistance, the alloy samples were supported on a glass slide in a fume cupboard about 25mm above the surface of 20% ammonium polysulphide solution so as to be exposed to the hydrogen sulphide that arises from that solution. All of the samples demonstrated good tarnish resistance during a one-hour test, with very slight yellowing after 45 minutes exposure to the hydrogen sulphide. The light film on the samples was easily removed with a cleaning cloth impregnated with stearyl mercaptan.

By way of comparison, a standard Sterling silver sample started to discolour as soon as it was subjected to the above test and after one hour had formed a heavy black tarnish which could not be removed with a cleaning cloth impregnated with stearyl mercaptan. The results obtained with a second Sterling silver sample that had been wiped with the cleaning cloth were similar and discoloration started as soon as the sample had been placed into the test. An Argentium Sterling alloy produced in accordance with EP-B-0729398 showed onset of tarnishing after 3 minutes. Another sample of the Argentium Sterling alloy that had been annealed in a selectively oxidizing atmosphere as disclosed in WO 02/09502 showed onset of tarnishing after 6 minutes. The markedly increased delay in onset of tarnishing was unexpected in the absence of an increased delay in the case of the standard Sterling Silver article.

## Example 2

### Effect of post-treatment solvent cleaning

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Example 1 was repeated for the Argentium samples except that instead of buffing with cotton wool after the mercaptan treatment, the samples were ultrasonically degreased in EnSolv 765 for 2 minutes. The samples were then tarnish tested as described in Example 1 and all found to show enhanced tarnish resistance. The ability of the protective effect of the stearyl mercaptan treatment to survive ultrasonic cleaning in EnSolv suggests that the tarnish resistance is

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being achieved by a surface reaction involving the stearyl mercaptan and possibly the germanium in the Argentium Silver, and not by formation of a grease or oil layer on the surface of the Argentium.

5

### Example 3

#### Aqueous dip application (solvent degreased samples)

10 An anti-tarnish treatment solution was prepared using the following ingredients:

	Stearyl mercaptan	1g
	EnSolv 765	5 ml
	Detergent (Fairy Liquid)	40 ml
15	De-ionised water	100 ml

20 The Stearyl Mercaptan was dissolved into the EnSolv 765 after which the resulting solution was mixed with detergent (Fairy Liquid) and diluted with water to provide an aqueous dip. Samples of Argentium silver were polished and ultrasonically degreased in EnSolv 765 for 2 minutes, immersed into the above aqueous dip for 2 minutes at ambient temperatures and then rinsed under running tap water. It was noted the water was immediately repelled from the polished surface, which left the samples dry. Samples were tarnish tested as described in

25 Example 1 and all showed enhanced tarnish resistance.

#### Example 4

##### Aqueous dip application 2 (detergent degreased samples)

5        Samples of Argentium Sterling were degreased in a 2% aqueous solution  
of a detergent (Fairy Liquid) and were then immersed in the treatment solution of  
Example 3. It was noted that the treated samples had become water-repellent as  
described in Example 3. Samples were tarnish tested as described in Example 1  
and all showed enhanced tarnish resistance. The above test was repeated except  
10       that the Fairy liquid in the treatment solution was replaced by a liquid hand soap  
(40 ml). When exposed to ammonium polysulphide solution, the samples did not  
show enhanced tarnish resistance. It is possible that this may have been because  
the hand soap was more dilute.

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#### Example 5

##### Simultaneous degreasing and anti-tarnish treatment

The following solutions were prepared:-

20

- 1 gram stearyl mercaptan
- 5 ml EnSolv 765
- 20ml detergent (Fairy Liquid)
- 100ml de-ionised water

25

- 1 gram stearyl mercaptan
- 5 ml EnSolv 765
- 30ml detergent (Fairy Liquid)
- 100ml de-ionised water

30

- 1 gram stearyl mercaptan (Preferred quantities)
- 5 ml EnSolv 765
- 40ml detergent (Fairy Liquid)
- 100ml de-ionised water

5

- 1 gram stearyl mercaptan
- 5 ml EnSolv 765
- 40ml detergent (Fairy Liquid)
- 500ml de-ionised water

10

- 1 gram stearyl mercaptan
- 5 ml EnSolv 765
- 40ml detergent (Fairy Liquid)
- 1000ml de-ionised water.

15

The solutions were heated to 50°C in an ultrasonic cleaning tank. Samples of polished Argentium Silver were ultrasonically degreased in the solutions for 2 minutes and were rinsed under running tap water. For the first three of the above treatment solutions, it was observed that water was repelled off of the surface leaving the samples dry. Samples treated with the first three solutions above were tarnish tested as described in Example 1 and all showed enhanced tarnish resistance. However, in the case of the samples treated with the last two solutions, water was not repelled off of the surface during the rinsing stage. When the samples dried they showed streaks on the surface which discoloured during the tarnish test. The sample treated with the 500ml solution showed less discolouration than the sample treated with the 1000ml solution. The above experiments show that Argentium silver can be simultaneously degreased and protected against tarnish using a thiol treatment agent applied in an aqueous system, and that the more concentrated the stearyl mercaptan/EnSolv/detergent/Water solution, the better the tarnish resistance produced.

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### Example 6

Direct "Sponge" Application - Neat Detergent Solutions (solvent degreased/  
5 aqueous degreased samples)

The following solutions were prepared:

- 1 gram stearyl mercaptan
- 10 - 5 ml EnSolv 765
- 40ml detergent (Fairy Liquid) (Preferred quantities)
  
- 1 gram stearyl mercaptan
- 5 ml EnSolv 765
- 15 - 40ml soap (liquid hand soap)

The stearyl mercaptan was initially dissolved into the EnSolv. The detergent was then mixed into the solutions. Samples of Argonium Silver were polished and ultrasonically degreased in EnSolv 765 for 2 minutes. The stearyl  
20 mercaptan/EnSolv/detergent solutions were then directly applied to the surface of the Argonium samples using damp cotton wool and massaged into lather. The samples were then rinsed under running tap water. In each case, it was noted that water was repelled off of the polished surface, leaving the samples dry. Samples were tarnish tested as in Example 1 by being exposed to neat ammonium  
25 polysulphide solution over a period of 1 hour. They all showed enhanced tarnish resistance. The above direct "sponging" method for applying the Stearyl Mercaptan was tested on samples degreased in a 2% Fairy Liquid aqueous solution. Enhanced tarnish resistance was again achieved.

**Example 7**

**Cloth Application (solvent degreased samples)**

5       Cloths were prepared by soaking clean cotton cloth in the following solutions:and allowing the cloths to dry

- 0.1 gram Stearyl Mercaptan dissolved in 100ml EnSolv
- 0.5 gram Stearyl Mercaptan dissolved in 100ml EnSolv
- 10       - 1.0 gram Stearyl Mercaptan dissolved in 100ml EnSolv (Preferred)

Samples of Argentium Silver (which had been polished and ultrasonically degreased in EnSolv 765 for 2 minutes) were wiped with the cloths then buffed with clean cotton wool. Samples were tarnish tested as described in Example 1  
15       by being exposed to ammonium polysulphide solution over a period of 1 hour. All of the samples showed enhanced tarnish resistance.



# CLAIMS

1. Use of an alkanethiol, alkyl thioglycollate, dialkyl sulfide or dialkyl disulfide for the surface treatment of an alloy of silver containing an amount of germanium that is effective to reduce fire-stain and/or tarnishing so as to reduce or further reduce tarnishing of the alloy such that a sample can be supported close above a 20% solution of ammonium polysulphide for at least 30 minutes while retaining a generally untarnished appearance.
2. The use of claim 1, wherein the alkanethiol, alkyl thioglycollate, dialkyl sulfide or dialkyl disulfide has C<sub>12</sub>-C<sub>24</sub> alkyl groups.
3. The use of claim 1 or 2, wherein the alkanethiol, alkyl thioglycollate, dialkyl sulfide or dialkyl disulfide is in an organic solvent.
4. The use of claim 3, wherein the solvent containing the alkanethiol, alkyl thioglycollate, dialkyl sulfide or dialkyl disulfide is generally neutral.
5. The use of claim 3 or 4, wherein the alkanethiol, alkyl thioglycollate, dialkyl sulfide or dialkyl disulfide is in a solvent based on n-propyl bromide.
5. The use of claim 3 or 4, wherein the alkanethiol, alkyl thioglycollate, dialkyl sulfide or dialkyl disulfide is in (a) a composition obtainable by dissolving said alkanethiol, alkyl thioglycollate, dialkyl sulfide or dialkyl disulfide in an organic solvent and adding to said solution a relatively concentrated aqueous soap or detergent, or (b) an aqueous dispersion obtainable by dissolving said alkanethiol, alkyl thioglycollate, dialkyl sulfide or dialkyl disulfide in an organic solvent, adding to said solution a relatively concentrated aqueous soap or detergent, and diluting the resulting mixture with water.

7. The use of claim 1 or 2, wherein the alkanethiol, alkyl thioglycollate, dialkyl sulfide or dialkyl disulfide is contained in a polish or impregnated into a polishing cloth.

5 8. The use of any preceding claim, wherein the alkanethiol or alkylthioglycollate is selected from stearyl mercaptan, cetyl mercaptan (octadecyl mercaptan) and stearyl thioglycollate and cetyl thioglycollate.

10 9. The use of any preceding claim, for the surface treatment of an alloy that further comprises a grain refiner.

10 The use of any preceding claim for the surface treatment of a ternary alloy of silver, copper and germanium.

15 11. The use of claim 10, wherein the ternary alloy consists, apart from impurities and any grain refiner, of 80-96% silver, 0.1-5% germanium and 1-19.9% copper, by weight of the alloy.

20 12. The use of claim 10, wherein the ternary alloy consists, apart from impurities and grain refiner, of 92.5-98% silver, 0.3-3% germanium, and 1-7.2% copper, by weight of the alloy, together with 1-40 ppm boron as grain refiner.

25 13. The use of claim 10, wherein the ternary alloy consists, apart from impurities and grain refiner, of 92.5-96% silver, 0.5-2% germanium, and 1-7% copper, by weight of the alloy, together with 1-40 ppm boron as grain refiner.

14. The use of any of claims 1-9 for the treatment of a quaternary alloy of silver, copper, zinc and germanium.

30 15. The use of claim 14, wherein the zinc is present in a ratio, by weight, to the copper of no more than 1:1.

16. The use of any preceding claim, wherein the alloy is in the form of a finished or semi-finished article.

5 17. Use of a  $C_{12}$ - $C_{24}$  alkanethiol, alkyl thioglycollate, dialkyl sulfide or dialkyl disulfide in the preparation of a tarnish inhibitor for an article of a silver/germanium alloy that has a silver content of at least 77 wt % and a germanium content of between 0.4 and 7%, the remainder principally being copper, so as to reduce tarnishing of the alloy such that a sample can be supported  
10 close above a 20% solution of ammonium polysulphide for at least 30 minutes while retaining a generally untarnished appearance.

18. An alloy of silver, or a shaped article formed of said alloy, containing an amount of germanium that is effective to reduce fire-stain and/or tarnishing and  
15 that has been treated with a  $C_{12}$ - $C_{24}$  alkanethiol, alkyl thioglycollate, dialkyl sulphide or dialkyl disulphide.

19. A method for manufacturing a tarnish-resistant silver article, which comprises the steps of:

20 forming a shaped article of an alloy of silver containing an amount of germanium that is effective to reduce fire-stain and/or tarnishing;

surface treating the article with an alkanethiol, alkyl thioglycollate, dialkyl sulphide or dialkyl disulphide; and

introducing the article into packaging.

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20. The method of claim 19, wherein said packaging includes a presentation box.

21. The method of claim 20, wherein the packaging includes external  
30 wrapping for the presentation box.

## ABSTRACT

### ENHANCING SILVER TARNISH-RESISTANCE

5           An alkanethiol, alkyl thioglycollate, dialkyl sulfide or dialkyl disulfide  
may be used to surface treat of an alloy of silver containing an amount of  
germanium that is effective to reduce fire-stain and/or tarnishing. The treatment  
has been found to further reduce tarnishing of the alloy such that a sample can be  
supported close above a 20% solution of ammonium polysulphide for at least 30  
10 minutes while retaining a generally untarnished appearance. The treatment may  
be carried out at the end of manufacturing a shaped article to give rise to an article  
that will preserve its untarnished appearance both during transit to a point of sale  
but during subsequent display for an extended period. The invention therefore  
also includes a method for manufacturing a tarnish-resistant silver article, which  
15 comprises the steps of forming a shaped article of an alloy of silver containing an  
amount of germanium that is effective to reduce fire-stain and/or tarnishing,  
surface treating the article with an alkanethiol, alkyl thioglycollate, dialkyl  
sulphide or dialkyl disulphide; and introducing the article into packaging.